U.PORTO
FACULDADE DE MEDICINA DENTÁRIA
UNIVERSIDADE DO PORTO

Patrícia Isabel Fernandes Leite

"The Application Of Graphene In Removable Prosthesis"

RESEARCH DISSERTATION

Porto
2015

U.PORTO
FACULDADE DE MEDICINA DENTÁRIA
UNIVERSIDADE DO PORTO

Research Dissertation

Integrated Master in Dental Medicine

"The Application Of Graphene In Removable Prosthesis"

Patrícia Isabel Fernandes Leite

ADVISOR: Patrícia Alexandra Barroso da Fonseca
Academic level- PhD in Dental Medicine by Faculty of Dental Medicine, University of Porto
Professional Title- Dentist

COADVISOR: Maria Helena Guimarães Figueiral da Silva
Academic level- Full Professor
Professional Title- Dentist

(Rua Dr. Manuel Pereira da Silva, 4200-393 Porto; Tlf: +351220901100)

Porto

Scientific area: Removable Prosthodontic/Dental Materials

“The greatest enemy of knowledge is not ignorance, it is the illusion of knowledge.”

Stephen Hawking

INDEX

ABSTRACT

Introduction: The removable dental prosthesis is often the only solution of oral rehabilitation that we can demand. The main materials used in its confection are metal alloys such as cobalt-chromium and acrylic resins, mainly polymethylmethacrylate. Nevertheless, these materials have weaknesses that compromise the function of prosthesis, and its fracture could happen.

In the last years, graphene has attracted great interest due to its exceptional physical, chemical, thermal and electrical properties. This material can be described as a single layer of pure carbon only one atom thick. Graphene is flexible, practically transparent, very strong and biocompatible. These unique characteristics make it a material with a range of practical applications, namely in biomedical areas.

Objectives: Test the use of graphene in arrangement with the materials used in confection of removable dental prosthesis.

Materials and Methods: A sample of polymethylmethacrylate resin acrylic and cobalt-chromium alloy was coated with a mono-layer of graphene which was synthesised by chemical vapour deposition on copper-foil enclosures.

Sixty test specimens of polymethylmethacrylate with different concentrations of graphene were also prepared and 30 used in impact strength tests and 30 in flexural strength tests. The collected data were introduced and analyzed in Microsoft® Excel program.

Results: It is successively possible include graphene (by coating and incorporation) in materials used for the fabrication of removable dental prosthesis. The values of the impact and flexural strength changed according to the percentage of graphene used and the best results were achieved with a graphene concentration of 1/5 and 1/4.

Conclusion: The promising properties together with the ease of processing and functionalization make graphene-based materials ideal candidates for incorporation into a variety of materials, including in dental medicine.

Keywords: graphene; removable dental prosthesis; mechanical properties; polymethylmethacrylate; cobalt-chromium alloy; impact strength; flexural strength

RESUMO

Introdução: A prótese dentária removível é, frequentemente, a única opção terapêutica de reabilitação oral a que podemos recorrer. Os principais materiais usados na confeção de próteses dentárias removíveis são as ligas metálicas de cromo-cobalto e as resinas acrílicas, principalmente o polimetilmetacrilato. No entanto, estes materiais apresentam inconvenientes que comprometem a função de uma prótese dentária removível e que podem levar à fratura da mesma.

Durante os últimos anos, o grafeno tem despertado um grande interesse devido às suas excecionais propriedades físicas, químicas, térmicas e elétricas. Este material é descrito como uma camada de carbono com um átomo de espessura sendo flexível, muito forte, praticamente transparente e biocompatível. Estas características únicas tornam-no um material com grande potencial de aplicações práticas, nomeadamente, em áreas biomédicas.

Objetivos: Testar o uso do grafeno em combinação com os materiais usados na confeção de próteses dentárias removíveis.

Materiais e métodos: Foi feito o revestimento de uma placa de resina acrílica e uma placa de cromo-cobalto com uma monocamada de grafeno. O grafeno usado foi sintetizado por deposição de vapor químico em folha de cobre.

Foram também realizadas 60 amostras de resina acrílica com diferentes concentrações de grafeno, 30 foram usadas em testes de impacto e 30 em testes de resistência à flexão. Os dados recolhidos foram introduzidos e analisados no programa *Microsoft® Excel*.

Resultados: Os resultados mostraram que é possível incluir com sucesso o grafeno (através do revestimento e da mistura) nos materiais usados na confeção de próteses dentárias removíveis. Os valores da força de impacto e flexão mudaram de acordo com a percentagem de grafeno usada e os melhores resultados foram encontrados para a concentração de 1/5 e 1/4 de grafeno.

Conclusões. As propriedades promissoras junto com a facilidade de processamento e funcionalização, tornam os materiais à base de grafeno candidatos ideais para serem incorporados numa variedade de materiais, incluindo na medicina dentária.

Palavras-chave: grafeno, prótese dentária removível, propriedades mecânicas, polimetilmetacrilato, liga de cromo-cobalto, resistência ao impacto, resistência à flexão

1. INTRODUCTION

1. Introduction

The removable dental prosthesis is often the only solution to replace missing natural teeth. It could be complete or partial and it is proposed to restore or improve oral functions as aesthetics, mastication, phonation and comfort. The main materials used in its confection are metal alloys such as cobalt-chromium and acrylic resins, mainly polymethylmethacrylate. The advantages of cobalt-chromium alloys are their lighter weight, greater stiffness and greater strength. For these reasons, they have been largely used for making removable partial prosthesis. However, the base metal alloys are extremely hard becoming the adjustments more difficult. On the other hand, the majority of complete prosthesis is fabricated using acrylic resins. The main advantage is the relatively easiness with which it can be processed and reduced cost. Thus, the physical properties of prosthesis base resins are critical to the fit and function of removable dental prosthesis.[1]

All dental materials must first be biocompatible, tolerating oral fluids and not releasing any injurious products into the oral environment, and then exhibit appropriate physical and mechanical properties to ensure adequate performance and long-term durability. [1]

An important factor in the design of a dental prosthesis is the strength, a mechanical property of a material which ensures that the prosthesis serves its intended functions effectively and safely over extended periods of time.[1] For this reason, some studies have been done with reinforced acrylic resins and new metal alloys to improve the strength of prosthesis. In the same pathway, news materials have been investigated for possible application in dental prosthesis.

Graphene is a new material that can meet the desirable features to be used for this purpose. A single two-dimensional layer in which the carbon atoms are presented in a sp2 connection and organized in a hexagonal mesh.[2,3] Graphene shows superior thermal, electrical and mechanical properties[4] including high fracture resistance, excellent mechanical strength, high Young's Modulus (1TPa)[5], high thermal and electrical conductivity and good thermal stability.[3] Furthermore, it is biocompatible, flexible, very light, it has a large surface area, it is practically transparent because it only absorbs 2.3% of the light, and at the same time it is very dense.[2,3,5-7]

Graphene specimens typically exist as monolayer attached to substrates made of another material or “free-standing graphene” (this means that a graphene sheet is isolated from its environment).[8] The purpose of this study was test the use of graphene specimens in arrangement with the materials used in confection of removable prosthesis and the research hypotheses were that graphene could improve the mechanical properties of these materials.

2. MATERIALS AND METHODS

2. Materials and Methods

2.1. Inclusions in the form of graphene monolayer attached to substrate

The graphene used for coating a sample of polymethylmethacrylate resin acrylic and cobalt-chromium alloy was synthesised by low-pressure chemical vapour deposition on copper-foil enclosures and was transferred using a polymethylmethacrylate coating likes substrate temporary in an electrochemical delaminating process.

For the graphene synthesis, 25µm thick of 99.999% pure copper foils were used. This procedure were observed 0,5mTorr and 1020 °C and was used methane as a carbon source and hydrogen which appears to serve a dual role: an activator of the surface bound carbon that is necessary for monolayer growth and an etching reagent that controls the size and morphology of the graphene domains. The flow rate was 1 and 30 minutes of time deposition (Figure 1. A).

In this procedure the polymethylmethacrylate layer acts as a supporting layer that prevents rolling or tearing of graphene during the transfer process. Polymethylmethacrylate can be easily spin coated on graphene grown with copper foil and moved to the final substrate.[5]

In an electrolytic cell, an aqueous solution of K2S2O8 was used as the electrolyte and polymethylmethacrylate/graphene/copper and platinum were used as the cathode and anode, respectively. Slight etching of copper together with hydrogen gas bubbles emerging between graphene and copper layer gently induces release of the polymethylmethacrylate/graphene. Afterwards graphene can be transferred and polymethylmethacrylate is washed away. Because the process involves only a minuscule amount of copper etching it can be reused for graphene growth (Figure 1. B). [5]

Graphene was then placed on the target substrates and left at 180 °C during 12 hours to gets dry. The polymethylmethacrylate layer was washed in acetone (Figure 1. C).

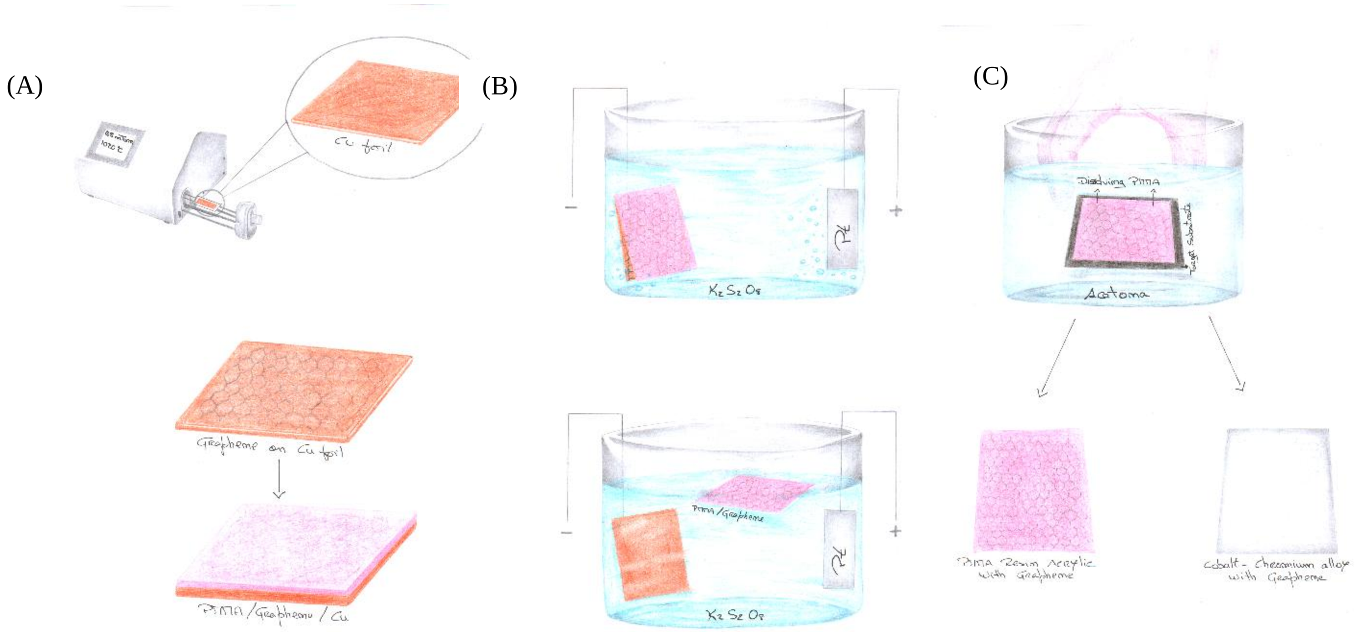


Figure 1. Graphene production by low-pressure chemical vapour deposition (A) and transfer using a polymethylmethacrylate coating (B and C).

2.2. Inclusions in the form of “Free standing Graphene”

The graphene used for mechanical tests was the pristine graphene monolayer flakes (dispersion in ethanol, concentration: 1 mg/L) , an ultrapure graphene with a carbon content of 99.99%, an average flake thickness of 0.35 nm (1 monolayer) and an average particle (lateral) size of ~ 550 nm (150-3000) nm. (Figure 2. A)

The acrylic resin used was an autopolymerized resin (megaCRYL), system powder (polymer) liquid (monomer). (Figure 2. B)

(B)

(A)

Figure 2. (A) Acrylic resin; (B) Pristine Graphene

Sixty specimens of acrylic resin, with different concentrations of graphene incorporated in the monomer, were made. Thirty samples had approximately 74 mm length, 9 mm width and 4 mm depth were used to flexural strength tests (Figure 3. A). The other thirty samples had 48 mm length, 4 mm width and 3 mm depth were used to impact tests (Figure 3. B). Each specimen was prepared by mixing the powder and liquid incorporating graphene in the monomer in different concentrations. The sixty specimens done were divided into five groups of twelve specimens each (six to each test). In the first group was used 1/5 of graphene, in the second group 1/4, in the third 1/3 and in the fourth group we used 1/2 of graphene. The control group (fifth group) was formed by twelve specimens of acrylic resin without graphene.

(A)

(B)

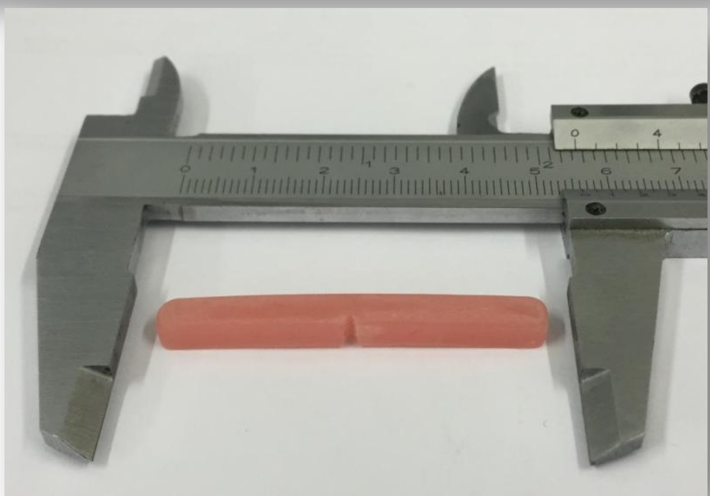


Figure 3. (A) Specimen for the flexural strength test; (B) Specimen for the impact strength test

For the confection of samples and, in order to obtained uniform results, a silicon key was done so that the dimensions, shape, and design be identical. The resin was manipulated in accordance with the producer's instructions (about one third of the mass is liquid monomer) and for each test were respected the ISO standards.

The samples obtained were used in impact and flexural strength tests.

2.2.1. Impact Strength Test

For the evaluation of the impact strength, it was used the Charpy´s pendulum test. For this case the Hounsfield Plastic Impact Machine, from Tensometer Ltd, Morland Road, Croydon (Figure 4) was used to evaluate the impact strength.

For the test, the specimen was positioned in the two supports of the machine, a 1/8 Lb weight was used, and it is release from a pre-determined height, which makes a pendulum movement and fractures the center of the samples in a horizontal position.

Figure 4. Impact strength test by Charpy method

2.2.2. Flexural strength test

Flexural strength test was performed by 3-point bending test using an Instron ElectroPuls E1000 testing machine (Porto Biomechanics Laboratory, Portugal), which can be seen in Figure 5.

The specimen was positioned in a support that has two outer loading pins and a central loading pin which is clamped in the load cell of the machine.

For the test it was applied a pre load of, approximately, 2N, and a crosshead speed of 5mm/min. For each test the force of the specimen was recorded as a function of the applied displacement of 15mm.

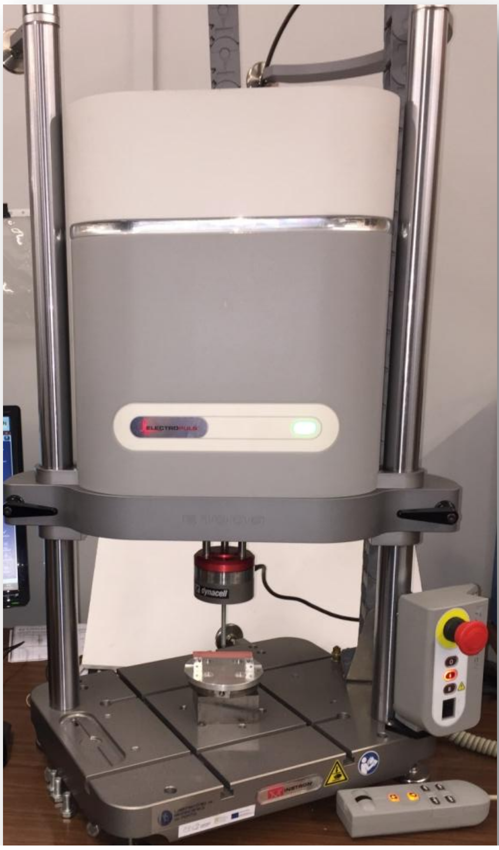


Figure 5. Flexural strength test by 3-point bending test

2.2.2.1. Fracture analysis

The fractures of the specimens broken by the three point bending tests were classified as brittle or ductile by visual inspection. When the fragments of specimens fractured could be repositioned at the fractured line presenting a smooth surface, the fractures were classified as brittle. Those presenting plastic deformation, exhibiting rough and jagged surfaces were recorded as ductile. [9]

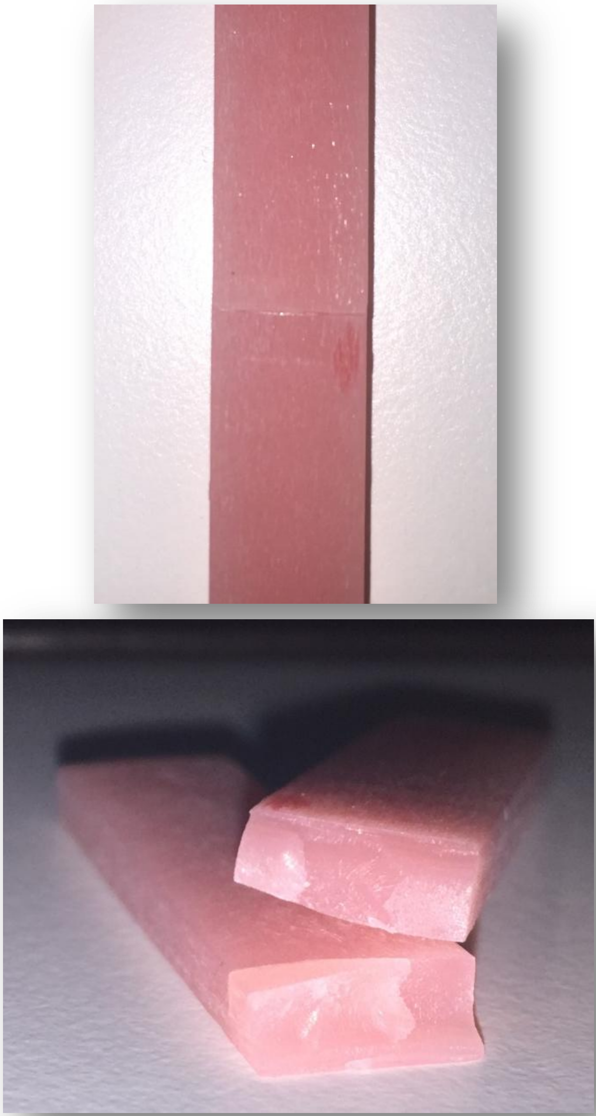
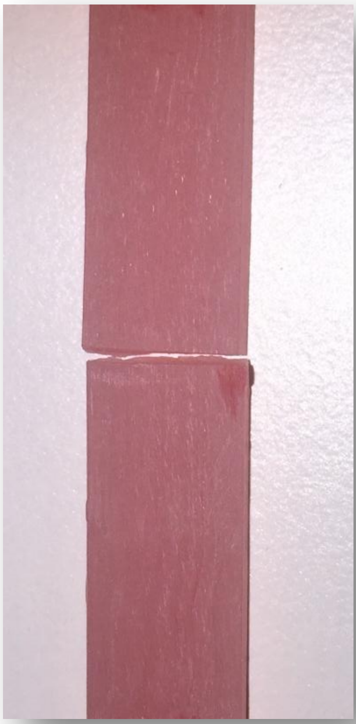


Figure 6. Brittle fracture



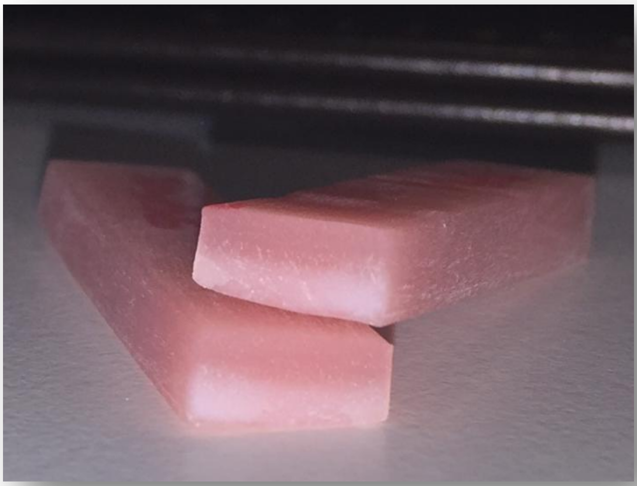


Figure 7. Ductile fracture

2.3. Data analysis

The data analyses were done using the Microsoft® Excel program.

3.RESULTS

3. Results

3.1. Inclusions in the form of graphene monolayer attached to substrate

The authors were able to successfully coat a sample of polymethylmethacrylate resin acrylic and cobalt-chromium alloy with a mono-layer of graphene (Figure 8).

(A) (B)

Figure 8. A sample of polymethylmethacrylate resin acrylic (A) and cobalt-chromium alloy (B) coats with a monolayer of graphene.

3.2. Inclusions in the form of "Free standing Graphene"

3.2.1. Impact Strength Test

Results of the impact strength test are displayed in Figure 9. It was verified that there was an improvement of impact strength value for the concentration of 1/5 and 1/4 of graphene.

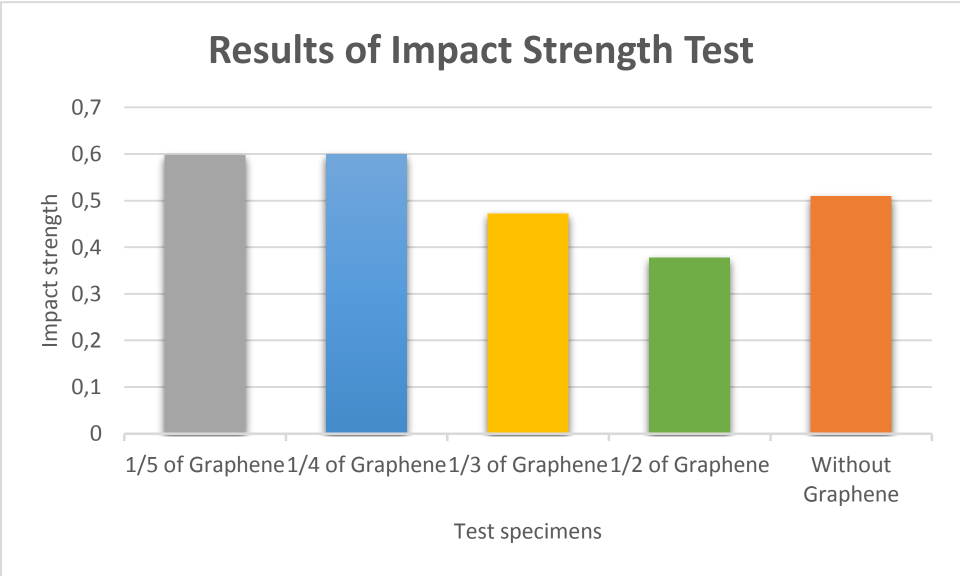


Figure 9. Results of Impact Strength Test

3.2.2. Flexural Strength Test

Results of the flexural strength tests are displayed in Figures 10, 11, 12 and 13.

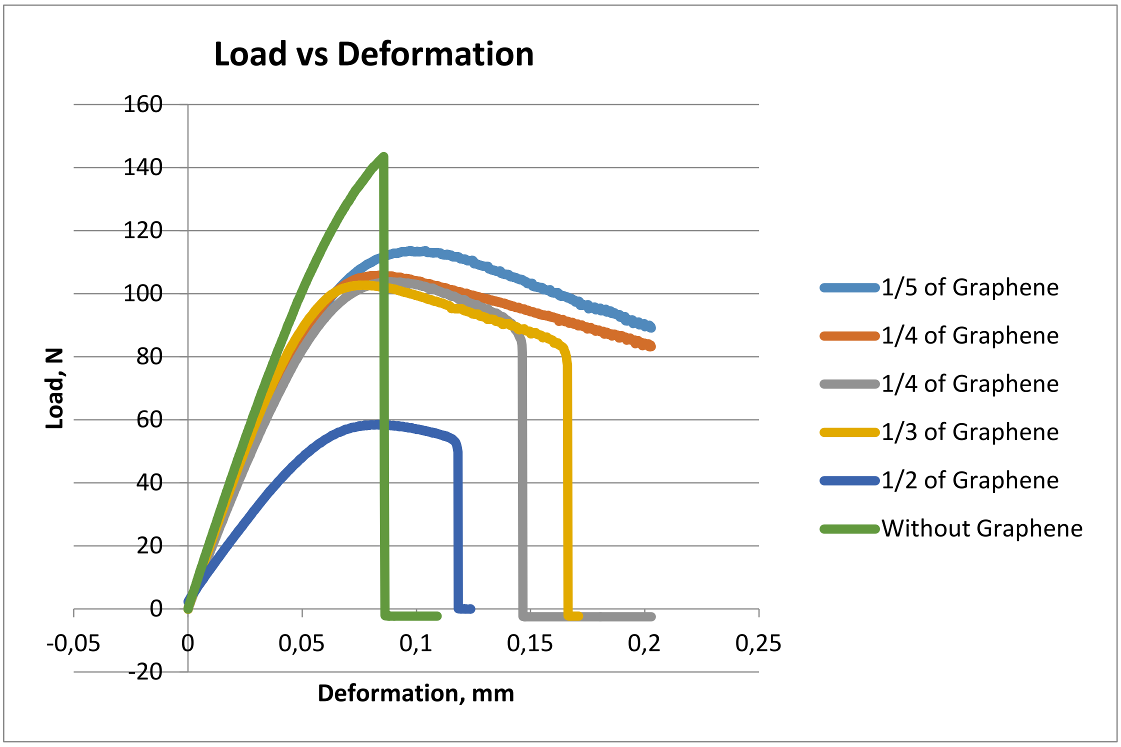


Figure 10. Load vs. Deformation graph for acrylic resin specimens tested

Specimens test	Maximum Load, N
1/5 of Graphene	113,0462
1/4 of Graphene	103,0099
1/3 of Graphene	102,004
1/2 of Graphene	58,0748
Without Graphene	143,4994

Figure 11. Maximum load supported by the specimens with different concentration of graphene until fracture or permanent deformation

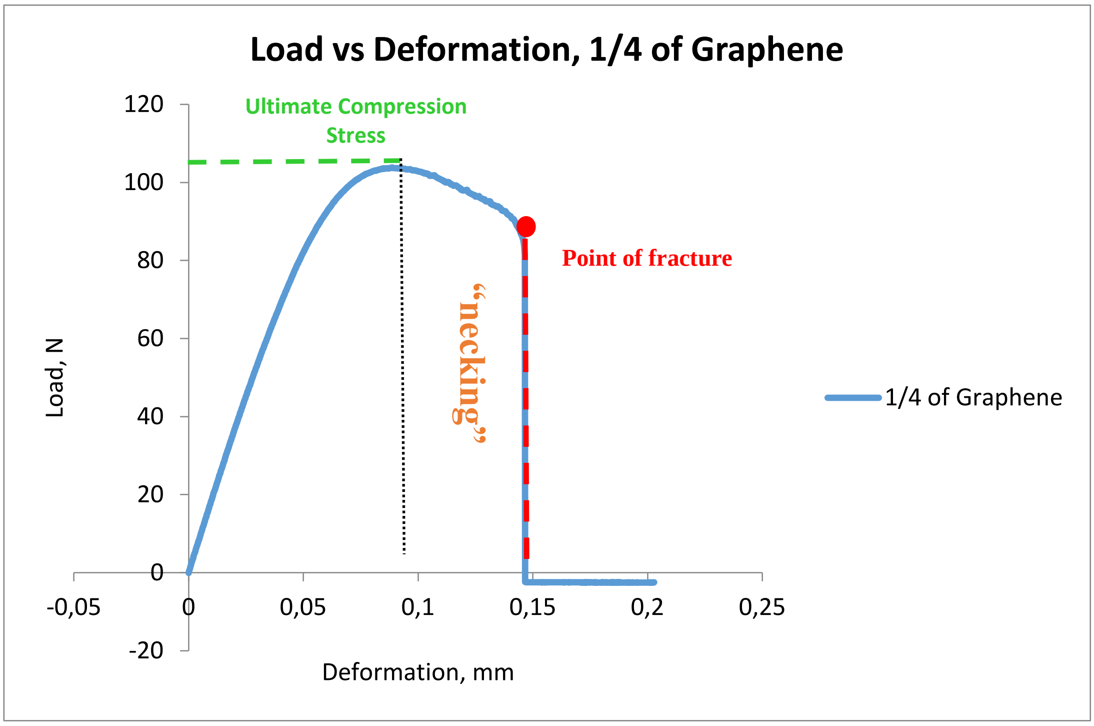


Figure 12. Graphs showing the existence of "necking"

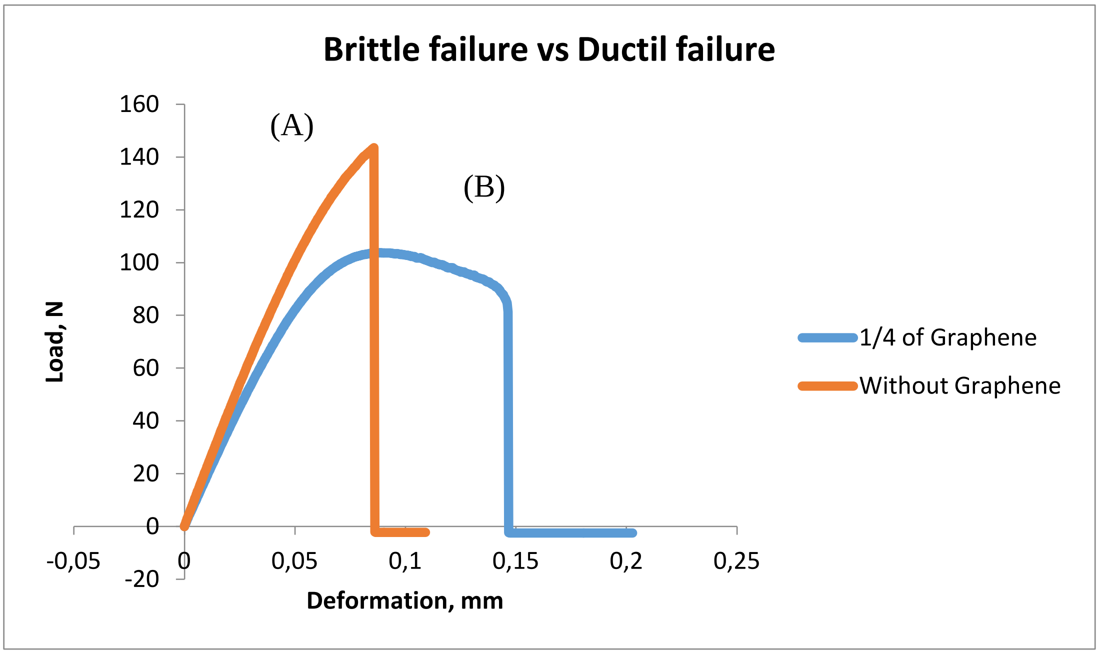


Figure 13 (A). Brittle failure, (B) Ductile failure

From the results showed in the graphs above we can verify that:

1. There were changes in the values of flexural strength according to the percentage of graphene incorporated. Contrary to our expectations, the graphene does not improve the flexural strength and, with the increases of graphene concentrations, the maximum load supported decreases. However, change the ductility of the material. Its magnitude can be assessed by the amount of permanent deformation indicated by the load-deformation curve.[1]

2. All the specimens with graphene incorporated showed the existence of necking, characteristic of ductile materials (Figure.12). Necking is a local deformation that begins at a tensile point or ultimate stress point. After ultimate stress is reached, the cross-sectional area of a small portion of the material decreases. Necking takes place after a material passes through the elastic, yielding, and strain hardening region of a material test.[15]

3. The specimens with graphene demonstrated a ductile failure. (Figure. 13)

4. The specimens without graphene demonstrated a brittle failure. (Figure.13)

In this figure 14 we can observe the action of compressive load in the flexural strength test of the specimen with 1/5 of graphene incorporated.

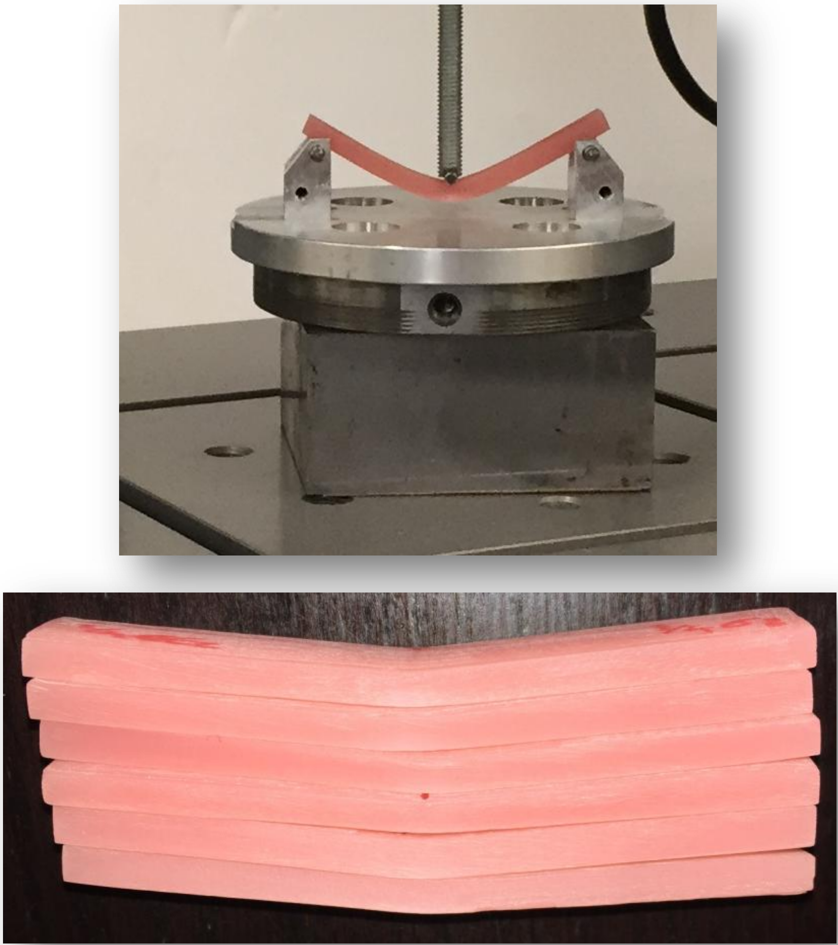


Figure 14. Action of compressive load in the flexural strength test

4. DISCUSSION

4. Discussion

Removable dentures are an economic treatment option for replacing missing teeth[10] and, although existing many ways, fixed or removable, to rehabilitate an edentulous or partial edentulous patient, there are specific indications for removable dentures: patients with severe periodontitis or excessive loss of alveolar bone, medically compromised and patients who are physically or emotionally vulnerable. Moreover, removable dentures can stand as a temporary solution waiting for more extensive treatment or as a definitive answer for patients who cannot afford an alternative.[11]

This study shows promising perspectives and practical strategies for possible applications of graphene in order to make the removable prosthesis a better treatment option.

Mechanical properties of removable denture are important for its clinical success and comfort of the patient.

The metal alloys used in confection of removable partial prosthesis should have a high elastic modulus and yield strength, in order to provide prosthesis rigidity and resistance to plastic deformation. The elastic modulus is a measure of stiffness of the alloy. The higher is the elastic modulus, the stiffer is the alloy. For a dental prosthesis, it is equivalent to its flexure resistance that provide adequate retention. Moreover, the hardness of the metal should be high enough to resist scratching and abrasion. Additionally, the alloy must be corrosion and tarnish resistant.[1]

Dental cobalt-chromium alloys are widely used for removable partial dentures because of their good mechanical properties and excellent corrosion resistance. The hardness of cobalt-chromium alloys is between 550 and 800 MPa and tensile strength 145 and 270

MPa.[12] However, the major problem of cobalt-chromium alloys are their low ductility, which can cause component fracture, particularly in the clasps and in the connectors of removable partial prosthesis.[1]

In the case of polymethylmethacrylate, resistance to impact fracture and high flexural strength are desirable properties of denture base acrylics.[1]

Polymethylmethacrylate is the material preferred for fabrication of complete dentures. It popularity is based on low cost, relative ease of use, reliance on simple processing equipment and aesthetic acceptable.[13] However, it is still far from ideal in satisfying the mechanical requirements of a prosthesis[14] and, there are some features of interest that can compromise physical and esthetic performance of a denture polymethylmethacrylate base that include polymerization shrinkage, porosity, water absorption, solubility, processing stresses, and crazing.[1]

With prosthesis bases in contact with mucosal surfaces, the transmission of a certain amount of thermal energy is desirable to transfer the sensations of heat and cold associated with food and beverages. The higher it is the thermal conductivity of a material, the greater the ability of a substance to transmit thermal energy and vice-versa. It is also desirable that the material exhibits good aesthetic, be availability, dimensional stability and easy of repair.[1]

Nevertheless, the fractures of dentures still are an unresolved problem, mostly, in acrylic resin dentures. There are various complications that can compromise the function of prosthesis and a failure fracture could happen not only related to design errors but also due the mechanical properties of the material used in its confection.[1,10,13] Fractures in dentures is a result of two different types of forces, specifically, flexural fatigue and impact. Both the flexural and impact strength are essential parameters that reflect the tendency of a denture base material to bear the functional masticatory and high impact forces when suddenly dropped by the patient. Flexural fatigue occurs after repeated flexing of a material and can be explicated by the development of microscopic cracks in areas of stress concentration that, with continued loading, fuse to a fissure that weakens the material. Impact strength of any material shows its resistance to total energy absorbed before it fractures.[14]

Crack initiation and propagation are essential to fracture. For engineering materials there are only two possible modes of fracture, ductile and brittle. The main difference between brittle and ductile fracture can be attributed to the amount of plastic deformation that the material undergoes before fracture occurs. In ductile failure, the cracks moves slowly and occur extensive plastic deformation. Crack is “stable” and resists further extension unless applied stress is increased. On the other hand, in a brittle failure, the crack propagates rapidly without increase in applied stress and there is no appreciable plastic deformation.[15]

Changes in the denture design or reinforcement of the base may improve the mechanical properties of the denture.

Graphene and its derivative materials have emerged as new biomaterials that offer the opportunity to develop a wide range of applications. The exceptional mechanical properties are of utmost importance for its requests, because they are highly needed in materials used in dental medicine.

Several methods of synthesis of graphene, production and transfer, have been developed. The production process defines its properties and as a result its applications.[4,16] After the discovery of graphene by mechanical exfoliation, several different synthesis methods such as chemical exfoliation, epitaxial growth, chemical oxidation and chemical vapour deposition, have been developed to improve the graphene quality and to produce it at a large scale.[5] Besides the reduction with chemical agents, electrochemical, photochemical and thermal reduction methods have been developed as well.[3]

After production, graphene needs be processing. The placement of graphene on arbitrary substrates is the key for its applications. Several transfer methods have been developed, but they all include limitations.[5,6] Although quality improvements can be made during the synthesis of graphene, it is important to note that most of the time degradation of quality occurs during the transfer process.[5] The methods of transfer are categorized into mechanical exfoliation, polymer-assisted transfer (polymethylmethacrylate), continuous transfer by roll-to-roll process, and transfer-free techniques including direct synthesis on insulating substrates.[5]

Functionalization is among the significant paths that drive graphene towards applications. Graphene modification can occur in two classes of locations: the basal plane and the edges and can be separated into four categories: functionalization with polymers, nanoparticles, atoms and biomolecules.[2,4] Graphene/polymer composites have attracted great interest because of their wide applications in high strength and conductive materials. Graphene is also a useful substrate for immobilizing nanoparticles to exhibit its high conductivity, large specific area and excellent thermal stability.[2] Once functionalized, the graphene-based nanostructures may open a gateway to new fields applications. The oxidized graphene sheet is one of the most important graphene forms, in which graphene is heavily oxygenated with a wide variety of oxygen species and because of this graphene oxides react easily with soluble moieties. This enables changing the hydrophilicity, hydrophobicity or organophilicity of graphene, as required for many applications.[4]

There are important qualities leading graphene to be considered as an ideal material in order to improve specific dental materials. Due to ultrahigh strength of graphene, its inclusions are effectively used in enhancement of both strength and fracture toughness.[8] Its large theoretical surface area which provides possibilities for its chemical functionalization, strong and flexible mechanical properties make graphene attractive for many applications and technologies.

The results demonstrated that graphene has potential to be used in dental materials, including in materials used for the fabrication of removable prosthesis.

However, it should be noted that there is no single method of graphene synthesis that yields graphene demonstrating the ideal properties for all potential applications.[2] Furthermore, the process of transfer introduces many steps in which graphene can be damaged. Development of transfer-free processes has become one of the most recent interests in this field.

In the chemical vapour deposition procedure that we used for coating a sample of polymethylmethacrylate and cobalt-chromium alloy, while it is possible to create high quality graphene at large-scale production, the successful separation of graphene from the substrate can introduce defects or rips in the product. It is not easy to achieve separation without damaging the structure of the graphene or affecting the properties of the material. This make this process expensive with a low yields,[2,17,18] but still is a very promising method for the synthesis of uniform, wafer size graphene layers.[2,17] Besides it is impractical if we need to wear surface like happens in the repairs of prosthesis.

The graphene solution added in the monomer didn't interfere with the polymerization of the acrylic resin when was used in the concentration of 1/5, 1/4 e 1/3. However with 1/2 of graphene incorporated the polymerization was affected. The time of polymerization increased and was not possible a homogeneous mixture occurring the appearance of resin lumps.

There were changes in the values of impact and flexural strength according to the percentage of graphene used.

Although graphene does not improve the flexural strength, it is capable to give ductility to the specimens. Ductility represents the ability of a material to sustain a large permanent deformation under a tensile load before it fractures.[1] The results of flexural strength test showed that the specimens with graphene have a ductile behavior, unlike the specimens without graphene that demonstrate being brittle. Ductile fracture is preferred in most design situations. First, brittle materials show little or no plastic deformation before fracture, and brittle fracture occurs very rapidly and without any warning. Ductile materials demonstrate extensive plastic deformation and energy absorption ("toughness") before fracture. This slows the process of fracture and offer time for the problem to be corrected. Second, because of the plastic deformation, more strain energy is needed to cause ductile fracture.[15]

Comparing with the specimens without graphene, there was an improvement of impact strength in the specimens with 1/5 and 1/4 of graphene. In the others, the values were lower.

Studies of mechanical properties exhibited by graphene are still in their infancy and there are important unsolved problems.[2,8] For example, the thickness and size have strong impacts on the properties and performance of graphene, but there is still lack of a scalable production method for synthesizing high quality graphene with controllable layer thickness and size. In order that graphene production evolves to an industrial scale, continuous improvement in scalable transfer methods is required in conjunction with reliable large-scale synthesis.[2] Some of the challenges proposed for graphene functionalization include the developing graphene-based materials with superior performance, the elimination of defects from graphene in order to open doors for promising new applications and providence a structural uniformity that are no dependent of the production method.[4]

The fact of the mechanical tests have not been performed in conditions similar to the oral cavity could be considered as a limitation of this *in vitro* study.

More tests should be conducted in order to better understanding the fracture and deformation mechanisms and to consolidate these exploratory observations.

5.CONCLUSION

5. Conclusion

Graphene is a material with outstanding mechanical and electronic properties that can meet the desirable features to be used in the confection of a removable dental prosthesis. Phrases such as the first two-dimensional material, single atomic thickness, incredible carrier mobility and mechanical strength have become the passport of graphene. The promising properties together with the ease of processing and functionalization make graphene-based materials ideal candidates for incorporation into a variety of materials.

Authors showed that graphene can be successfully used in removable prosthesis confection in order to improve mechanical properties of the materials, manly the polymethylmethacrylate. Although more studies are needed, the results obtained in this investigation are very encouraging.

References

1. Anusavice KJ, Shen C, Rawls HR. Phillips' science of dental materials. 12nd ed. Elsevier Health Sciences, 2012, p. 48-68, 367-95, 474-98.

2. Chen X, Wu G, Jiang Y, Wang Y, Chen X. Graphene and graphene-based nanomaterials: the promising materials for bright future of electroanalytical chemistry. Analyst. 2011; 136(22):4631-40.

3. Huang X, Yin Z, Wu S, Qi X, He Q, Zhang Q, Yan Q, Boey F, Zhang H. Graphene-Based Materials: Synthesis, Characterization, Properties, and Applications. Small. 2011; 7(14): 1876-902.

4. Yan L, Zheng YB, Zhao F, Li S, Gao X, Xu B, Weiss PS, Zhao Y. Chemistry and physics of a single atomic layer: strategies and challenges for functionalization of graphene and graphene-based materials. Science. 2012; 41(1):97-114.

5. Kang J, Shin D, Bae S, Hong BH. Graphene transfer: key for applications. Nanoscale. 2012; 4(18):5527-37.

6. Bonaccorso F, Lombardo A, Hasan T, Sun Z, Colombo L, Ferrari A. Production and processing of graphene and 2d crystals. Materials Today. 2012 Dec; 15(12):564-89.

7. Cui X, Zhang C, Hao R, Hou Y. Liquid-phase exfoliation, functionalization and applications of graphene. Nanoscale. 2011; 3(5):2118-26.

8. Ovid'ko IA. Mechanical properties of graphene. Reviews on Advanced Materials Science. 2013; 34:1-11.

9. Faot F, Panza LH, Garcia RCR, Cury AADB. (2009). Impact and flexural strength, and fracture morphology of acrylic resins with impact modifiers. The open dentistry journal.2009; 3(137).

10. Bilhan H, Erdogan O, Ergin S, Celik M, Ates G, Geckili O. Complication rates and patient satisfaction with removable dentures. The journal of advanced prosthodontics. 2012; 4(2): 109-115.
11. Wöstmann B, Budtz-Jørgensen E, Jepson N, Mushimoto E, Palmqvist S, Sofou A, Owall B. Indications for removable partial dentures: a literature review. The International journal of prosthodontics. 2006 (18): 139-45.
12. Carek A, Zivko BJ, Schauperl Z, Badel T. (2011). Mechanical Properties of Co-Cr Alloys for Metal Base Framework. International Journal of Prosthodontics and Restorative Dentistry. 2011; 1(1):13-19.
13. Meng TR, Latta MA. Physical properties of four acrylic denture base resins. The Journal of Contemporary Dental Practice. 2005 6(4): 93-100.
14. Jagger DC, Harrison A, Jandt KD. The reinforcement of dentures. Journal of oral rehabilitation. 1999; 26(3): 185-194.
15. Shackelford JF. "Introduction to materials science for engineers." 7nd ed. Pearson International Edition, 2005, p.240-61.
16. Rao CNR, Subrahmanyam KS, Matte HSSR, Abdulhakeem B, Govindaraj A, Das B, Kumar P, Ghosh A, Late DJ. A study of the synthetic methods and properties of graphene. Science and Technology of Advanced Materials. 2010;11(5).
17. Hiura H, Lee M, Tyurnina A, Tsukagoshi K. Liquid phase growth of graphene on silicon carbide. Carbon. 2012; 50(14):5076-5084.
18. Howsare CA, Weng X, Bojan V, Snyder D, Robinson JA. Substrate considerations for graphene synthesis on thin copper films. Nanotechnology. 2012; 23(13):1356

Acknowledgements

To my mom and dad
Thanks for all the support and love over these academic years. Thanks for everything you´ve done for me and for being so perfect.

To Professor Patrícia Fonseca and Professor Maria Helena Figueiral
For the availability, collaboration and shared knowledge

To Professor José Reis Campos
For the help and attention provided

To my sister, Célia Leite
For the darling, advices and courage

To my boyfriend, Diogo Vieira
For the care and support and for never letting me go down

To my cousin, David Leite
For being my brother and for never letting me forget who I am

To my friends
For the shared experiences and for always being there for me

To the dental technicians, Fernando Faria, Américo Ribeiro, José Torres
For the collaboration provided

To Engineer Nuno Viriato and Professor Mario Vaz
For all the help and availability supplied

To *Laboratório Ibérico Internacional de Nanotecnologia*
For all the support

APPENDIX

U. PORTO

FACULDADE DE
MEDICINA DENTÁRIA
UNIVERSIDADE DO PORTO

Declaração de autoria do trabalho apresentado

Monografia de Investigação/Relatório de Atividade Clínica

Porto, 1 de junho de 2015

Declaro que o presente trabalho, no âmbito de Monografia de Investigação/Relatório de Atividade Clínica, integrado no MIMD, da FMDUP, é da minha autoria e todas as fontes foram devidamente referenciadas.

A investigadora,

Patrícia Isabel Fernandes Leite

Patrícia Isabel Fernandes Leite

U.PORTO
FACULDADE DE MEDICINA DENTÁRIA
UNIVERSIDADE DO PORTO

Porto, 1 de junho de 2015

Parecer do Orientador

(Entrega do trabalho final de Monografia)

Informo que o trabalho de Monografia desenvolvido pela estudante Patrícia Isabel Fernandes Leite com o título: "The application of graphene in removable prosthesis" está de acordo com as regras estipuladas na Faculdade de Medicina Dentária da Universidade do Porto, foi por mim conferido e encontra-se em condições de ser apresentado em provas públicas.

A Orientadora,

Patrícia Alexandra Barroso da Fonseca

(Profª. Doutora Patrícia Alexandra Barroso da Fonseca)

U.PORTO

FACULDADE DE MEDICINA DENTÁRIA
UNIVERSIDADE DO PORTO

Porto, 1 de junho de 2015

Parecer do Coorientador
(Entrega do trabalho final de Monografia)

Informo que o trabalho de Monografia desenvolvido pela estudante Patrícia Isabel Fernandes Leite com o título: "The application of graphene in removable prosthesis", está de acordo com as regras estipuladas na Faculdade de Medicina Dentária da Universidade do Porto, foi por mim conferido e encontra-se em condições de ser apresentado em provas públicas.

A Coorientadora,

Maria Helena Guimarães Figueiral da Silva

Profª. Doutora Maria Helena Guimarães Figueiral da Silva